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Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass

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ABSTRACT

The equilibrium moisture content (EMC) of raw lignocellulosic biomass, along with four samples subjected to thermal pretreatment, was measured at relative humidities ranging from 11% to 97% at a constant temperature of 30 °C. Three samples were prepared by treatment in hot compressed water by a process known as wet torrefaction, at temperatures of 200, 230, and 260 °C. An additional sample was prepared by dry torrefaction at 300 °C. Pretreated biomass shows EMC below that of raw biomass. This indicates that pretreated biomass, both dry and wet torrefied, is more hydrophobic than raw biomass. The EMC results were correlated with a recent model that takes into account additional non-adsorption interactions of water, such as mixing and swelling. The model offers physical insight into the water activity in lignocellulosic biomass.

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1. Introduction

The moisture content of lignocellulosic biomass is of significant interest, when considering thermochemical conversion to fuels, e.g., by gasification or pyrolysis (Tester et al., 2005; US Department of Energy (DOE), 2008). In pyrolysis, the presence of moisture increases the yield of char, but for tar formation moisture has a dual role suppressing or enhancing depending on the pyrolysis temperature and ash content (Gray et al., 1985). A limited amount of moisture is beneficial in gasification, as the steam generated can influence the chemistry (by water gas shift reactions), increasing the Hydrogen content of the product synthesis gas. On the other hand, too much moisture increases the costs of thermochemical conversion, (Singh, 2004), since the moisture is first evaporated, rendering the process as an expensive dryer. A clear understanding of the factors influencing biomass equilibrium moisture content (EMC) will aid the commercialization of biomass conversion processes.

In general, moisture plays a fundamental role on the properties and behavior of any biologically derived material (Vasquez and Coronella, 2009). Dry biomass is much more stable and exhibits reduced rates of biological deterioration. It is well established that a change in a material's moisture content is influenced by a change in the relative humidity surrounding the material at constant temperature (Gronvall, 2006). EMC of biomass is defined as the moisture content in the biomass which is in thermodynamic equilibrium with the moisture in the surrounding atmosphere at a given relative humidity, temperature, and pressure.

Although the temperature and relative humidity of the surrounding air are the main factors controlling EMC, it may also be affected by the variety and composition of biomass, mechanical handling and previous moisture history (Silakul and Jindal, 2002). Knowledge of the relationship between the air relative humidity and moisture content of the lignocellulosic material is essential (Cordeiro et al., 2006). Understanding moisture content is important to design and control thermochemical conversions processes and control the final quality of the products (Bellur et al., 2009).

Throughout the biofuels literature, many papers have been written on biomass pretreatment. Most have the focus of producing soluble sugars from biomass, for subsequent biochemical conversion to fuels. Mosier et al. (2005) review those technologies, including steam explosion, lime pretreatment, acid pretreatment, and ammonia fiber explosion (AFEX). However, the needs for thermochemical conversion are different, and the emphasis is on producing a solid fuel that is relatively homogenous, regardless of origin, and one with increased fuel density, in order to enhance feedstock logistics. Torrefaction is a process for pretreating biomass well suited for subsequent thermochemical conversion (Bergman et al., 2005; Funke and Ziegler, 2009; Yan et al., 2009a). The effects of two distinct thermal pretreatment technologies, i.e., wet torrefaction and dry torrefaction, on EMC are investigated in this study.

Wet torrefaction of loblolly pine was performed in hot compressed water at temperatures ranging from 200 to 260 °C. The

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Nomenclature

Symbols

EMC	Equilibrium moisture content
H_R	Relative humidity
σ	Adsorption capacity parameter
χ	Flory–Huggins parameter
$\Delta\varepsilon$	Molecular potential energy parameter
v_{pw}	Specific volume ratio of biomass solid to water
α	Water adsorbed, bonded
θ	Water adsorbed, non bonded
Φ	Bio solids volumetric fraction
W_e	Weight of sample at equilibrium
W_d	Weight of completely bone dry sample
ΔF	Contribution to the chemical potential in the non-bonded phase due to mixing and swelling

reactor pressure was not controlled but indicated by a pressure gauge and ranged from 200 to 700 psi, approximately in accord with the water vapor pressure (Yan et al., 2009a). On the other hand, dry torrefaction, sometimes called low-temperature pyrolysis, is a process in which the biomass is heated in an inert gas environment (usually nitrogen) at temperatures ranging from 200 to 300 °C (Bergman et al., 2005). In both cases, previous researchers (Bergman et al., 2005; Kobayashi et al., 2009) indicated that the solid product has increased hydrophobicity relative to the feedstock.

In this work, we experimentally determine the EMC at relative humidities ranging from 11% to 97% at a single temperature (30 °C). The measured EMC were correlated with a recent model (Vasquez and Coronella, 2009). This particular model is based on physical and chemical principles, and offers an approach different from many other EMC models which are generally empirical. Fitting the measured data to the model gives some insight into water activity in pretreated biomass.

2. Methods

The static desiccator technique (Bellur et al., 2009) was used to measure the EMC of raw and pretreated lignocellulosic biomass (raw loblolly pine) by exposing the solid samples to constant relative humidities maintained by saturated salt solutions.

2.1. Sample preparation

Loblolly pine (Alabama, USA) was acquired and used in all EMC measurements. Fiber analysis of the raw biomass was measured by the van Soest method, with the following results: 11.9% hemicellulose, 54.0% cellulose, 25.0% lignin, 8.7% extractives, and 0.4% ash (Yan et al., 2009a). Pretreated biomass samples were produced according to the methods described by Yan et al., 2009a. All salts were reagent grade and purchased from Fisher Scientific.

2.2. Containers and salt solution

Biomass samples weighing about 3 g were placed in a Petri dish and then into transparent jars containing salt solutions. Each dish was placed on top of a plastic stand inside the jar to keep it separated from the saturated aqueous salt solutions at the bottom of the jars, and a canning lid sealed the jars. A total of eight different kinds of salts were used, with equilibrium humidity ranging from 11.3% (LiCL) to 97.0% (K_2SO_4). Equilibrium humidities of saturated salt solutions are available in the literature (Greenspan, 1977). The salt solutions were prepared by dissolving the salt crystals in distilled water at room temperature. Excess salt was added to saturate the solutions and to ensure constant relative humidity conditions (Acharjee, 2010).

The jars were placed in a water bath at constant temperature of 30 °C. The time for the samples to reach equilibrium varied from 9–15 days depending on pretreatment conditions, and especially on the relative humidity in the jar. A sample was assumed to be in equilibrium when three consecutive weight measurements showed a difference less than 1 mg. The moisture of the sample was determined by oven drying at 105 °C for 24 h.

3. EMC modeling

Various kinds of models have been proposed, both semi-empirical and empirical. Van den Berg and Bruin (1981) report in a literature review a list of 77 isotherm models that have been applied to biological materials, including wood and other fibrous materials. They classified these into four general categories: localized monolayer sorption models, multilayer sorption models, sorption models used in polymer science, and empirical models. Generally, sorbed water is said to consist of two phases: bonded, or strongly adsorbed, and free, or non-bonded. Chung-Pfost, Modified Henderson, Modified Halsey, and Modified Oswin model are considered standard models for fitting EMC experimental data by the American Society of Agricultural Engineers (Bellur et al., 2009).

Vasquez and Coronella (2009) proposed a model to describe equilibrium moisture in heterogeneous biomass substrates that provides additional physical insight into the water activity in this type of substrate. This model is based on combining standard molecular thermodynamic approaches and statistical mechanics to model EMC as a function of water activity in heterogeneous biomass substrates. The model attempts to take into account both bonded and non-bonded interactions of the water with the substrate. In this model, three phases of water are in thermodynamic equilibrium: the surrounding air and two phases in the biomass (bonded and non-bonded water). By bonded water, we mean water bonds strongly to the network through adsorption mechanisms, and by non-bonded, we mean condensed water still in the biomass phase, but it is absorbed in a weaker bonding to the biomass (relative to water in the bonded phases.) Thus, the EMC of the biomass is the sum of the bonded or adsorbed water (θ) plus non-bonded water, i.e., the water in the non adsorbed phase (α). At equilibrium, the following two equations are obtained:

$$\theta(\alpha+\theta)\exp(\Delta\varepsilon)=\alpha(\sigma-\theta)\exp(\Delta F) \tag{1}$$

$$(\alpha+\theta)H_R=\alpha\exp(\Delta F) \tag{2}$$

where

$$\Delta F=\ln(1-\phi_p)+\phi_p+\chi\phi_p^2+v_{pw}(\phi_p^{1/3}-\phi_p^{5/3}) \tag{3}$$

The model includes four adjustable parameters: σ describes the water adsorption capacity of θ (bonded) phase; $\Delta\varepsilon$ characterizes the difference in potential energy of water in the bonded phase with respect to pure water; χ is the Flory–Huggins interaction parameter; and v_{pw} is the average specific volume ratio of biomass to water in the biomass volumetric fraction used to find ϕ_p:

$$\phi_p=\frac{v_{\mathrm{pw}}}{(\alpha+\theta)+v_{\mathrm{pw}}} \tag{4}$$

ϕ_p describes the relative volume of biomass to water in the Flory–Huggins framework. Interested readers are directed to Vasquez and Coronella (2009) for additional details.

Eqs. (1) and (2) determine the isothermal value of EMC $\omega = \alpha + \theta$ as a function of the water activity in the gas phase, i.e., the relative humidity. To model the EMC, appropriate parameter values are found from experimental measurements of EMC. We used the least-squares sum of the residuals between experimental measurements and predicted values of the EMC. For this analysis, the Levenberg–Marquardt algorithm was used to minimize the objective function Φ given by:

$$\Phi(\chi, \Delta\varepsilon, \upsilon_{\text{pw}}, \sigma) = \sum_{i=1}^{N} (\text{EMC}_{i,\text{exp}} - \text{EMC}_{i,\text{mod}})^2 \tag{5}$$

The regression analysis was repeated several times with different initial values of the parameter set to confirm the validity of the regression parameters (Silakul and Jindal, 2002). The goodness of fit of the model was evaluated in terms of the root mean squares error (RMSE), the coefficient of determination (R^2) and residual sum of squares (RSS), and residual distribution plots. When available, the nature of biomass helps determine initial estimates of the parameters. Bellur et al. (2009) suggest some useful guidelines. In this model, σ refers the fraction of the adsorption capacity of biomass and it should be less than 1. The Flory–Huggins parameter χ, which determines compatibility of water and biomass, should be much greater than 0.5 because below this point, polymer and solvent are completely miscible (Ovejero et al., 2007). The energy parameter for adsorption, $\Delta\varepsilon$, should be close to the dimensionless heat of solidification of water in magnitude (-2.54). The total EMC (ω), sum of the adsorbed (bonded) water (θ) plus the water in non adsorbed phase (non-bonded) (α), should be less than 1 (as a function of the total water in the system).

4. Results and discussion

The EMC of a sample at a particular relative humidity was calculated as follows:

$$\text{EMC} = \frac{(W_e - W_d)}{W_d} \tag{6}$$

where W_e is the weight of the sample at equilibrium and W_d is the weight of bone dry sample weight. In this study, equilibrium was attained in 9–15 days. EMC measurements of raw biomass and of wet-torrefied biomass at $H_R = 11.3\%$ and $H_R = 83.6\%$ were duplicated, to test for reproducibility. The results are shown in Table 1. Generally, the EMC measurements are reproducible within ±0.5%.

Fig. 1 shows the dependence of EMC on relative humidity in raw loblolly pine, and on thermally pretreated loblolly. Most biological products exhibit a characteristic sigmoidal isotherm, such as that shown in Fig. 1 (Mankower and Dehority, 1943; Bjork and Rasmuson, 1995). At low H_R, EMC increases rapidly with H_R, followed by a period of more gradual increase, and then at high H_R, the EMC increases quite rapidly. Thermal pretreatment affects significantly the EMC of pretreated wood for all pretreatment conditions studies: 200, 230 and 260 °C for wet torrefaction, and 300 °C for dry torrefaction. The EMC of pretreated biomass decreases with increasing pretreatment temperature, and wet torrefaction produces a solid more hydrophobic than the one produced by dry torrefaction. For example, at 84% H_R, the EMC of raw biomass is 15.6%, but decreases to 5.3% after wet torrefaction at 260 °C, and to 8.7% after dry torrefaction at 300 °C.

Table 1
EMC of raw biomass feedstock and thermal pretreated solid products. Biomass feedstock is loblolly pine. H_R is relative humidity. Each of these EMCs was measured twice, with the range indicated by a high and low value.

Pretreatment	Treatment temperature (°C)	EMC (%) at H_R = 11.3%	EMC (%) at H_R = 83.6%
Raw biomass	–	3.5 ± 0.5	15.6 ± 0.9
Hydrothermal pretreatment	200	1.8 ± 0.5	12.8 ± 0.7
	230	0.9 ± 0.3	8.2 ± 0.7
	260	0.4 ± 0.3	5.3 ± 0.03

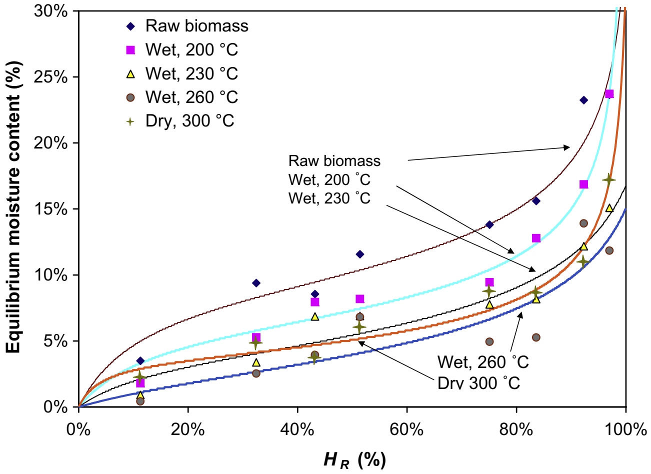

Fig. 1. EMC of raw biomass and treated biomass. Measured data are shown as points: ♦ raw biomass; ■ treated in water at 200 °C; ▲ treated in water at 230 °C; ● treated in water at 260 °C; ✦ treated in nitrogen at 300 °C. Results of the model presented in Eqs. (1) and (2) are also shown for each condition, as labeled.

The level of scatter of EMC data is higher than that indicated by the reproduced measurements shown in Table 1, likely indicating random experimental error. Although the measurements were done as carefully as possible, there are various sources of error. A significant potential source of random error is the slow growth of fungi in the constant-temperature jars. Small growths of fungi were visible on several the biomass samples at the completion of the EMC experiment. Biomass samples are susceptible to mold growth on the wood surface, due to the formation of hemicellulose-degradation products (e.g., sugars) during heat treatment. The environment of EMC experiments (humid at 30 °C) is suitable for the mold growth (Boonstra, 2008). The EMC measurements require extended time periods, as long as two weeks. Fungi has its own EMC distinct from woody biomass, and its growth may affect the structure of the woody biomass, at least on the surface.

All isotherms were fitted to the model given in Eqs. (1) and (2) and the results are also shown in Fig. 1. The fitted parameters and goodness of fit evaluations are shown in Table 2, and discussed below in Section 4.4.

4.1. Relationship of bonded and non-bonded water

Fig. 2 shows the isotherms for total moisture (EMC), bonded water, and non-bonded water. The isotherms were calculated from

Table 2
Fitted values of the coefficients of the model shown in Eqs. (1) and (2), along with several measures of model fitness, including RMSE (root mean squares error), the correlation coefficient R^2, and the residual sum of squares.

Parameter	Raw loblolly	Dry torrefaction 300 °C	Wet torrefaction		
			200 °C	230 °C	260 °C
σ	0.099	0.037	0.070	0.043	0.033
χ	3.067	1.798	2.636	1.479	1.206
ν_{pw}	0.146	0.097	0.113	0.163	0.152
$\Delta\varepsilon$	−2.126	−3.179	−1.994	−1.907	−1.122
RMSE	0.016	0.009	0.009	0.012	0.021
R^2	0.900	1.007	0.943	0.918	0.806
RSS	0.042	0.016	0.040	0.014	0.015

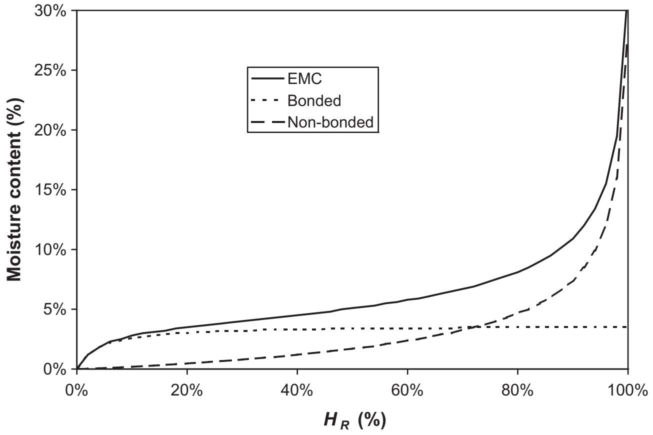

Fig. 2. Isotherms and partitioning for moisture in raw loblolly pine, predicted by the model given in Eqs. (1) and (2).

the model given in Eqs. (1) and (2), using the fitted parameter values for raw loblolly pine, given in Table 2. At low H_R, the total amount of moisture is essentially equal to the amount of adsorbed water. At H_R above 20%, the bonded water is nearly independent of humidity. The constant isotherm for bonded water at H_R greater than 20% indicates that the adsorbed phase is fully saturated, consistent with single-layer adsorption. Bjork and Rasmuson (1995) showed that the monolayer sorption saturation is reached at equilibrium moisture fractions in the range 0.04–0.06. The isotherm of bonded water shown in Fig. 2 is close to this range. The amount of non-bonded water is quite small at lower humidity and then it increases with humidity; above H_R = 80%, it increases rapidly.

4.2. Effect of pretreatment on bonded water

Moisture in wood is bound, or held, by intermolecular attraction within cell walls (Wiedenhoeft, 2010). Fig. 3 shows the effect of pretreatment on bonded water. After thermal pretreatment, biomass contains less bonded water. That means there are potentially significant changes in the structure of wood during pretreatment. Moreover, high temperature treatment makes biomass less hydrophilic, in terms of bonded water, compared to low temperature treatment. In Fig. 3, the bonded water decreases with the increase in pretreatment temperature.

4.3. Effect of pretreatment on non-bonded water

In cell lumens and cavities, non-bonded (non-adsorbed) moisture can exist as liquid water or water vapor. When the lumen volume decreases, there is less space available for either liquid or vapor (Wiedenhoeft, 2010). As seen in Fig. 4, pretreatment has little effect on the non-bonded water. Non-bonded water increases with H_R for all samples. But at any specific H_R, the content of non-bonded water is relatively independent of thermal pretreatment.

4.4. Parameter analysis and discussion

The parameters obtained by fitting the EMC model given in Eqs. (1) and (2) are given in Table 2, as a function of the pretreatment conditions. The adsorption capacity parameter, σ, is reduced by thermal pretreatment. For raw biomass, $\sigma = 0.1$, and is reduced with increasing pretreatment temperature, to $\sigma = 0.03$ for wet carbonization, and to $\sigma = 0.04$ for dry torrefaction. This indicates that the availability of adsorption sites is reduced with increasing pretreatment temperature.

Of the three primary components of lignocellulosic biomass, hemicelluloses have the greatest capacity for water sorption, while lignin has very little capacity for water sorption (Bjork and Rasmuson, 1995). In wet torrefaction, the hemicellulose is nearly completely removed at 200 °C, and is completely reacted at 230 and 260 °C (Yan et al. 2009a). Also note that both cellulose and lignin are partially reacted by hot water, and the extent of reaction increases with temperature. The sugars, which are degradation products of hemicellulose and cellulose, are deposited onto the pores of the solid, and after drying, are remain in significant quantities of these compounds (Yan et al. 2009a). The cellulose and lignin percentages of pretreated sample at 230 °C are 44.1% and 30.2%, whereas at 260 °C these percentages are 33.9% and 33.8% respectively (Yan et al. 2009a). Due to the relatively significant reduction of cellulose and relatively small change in lignin, pretreated solid at 230 °C adsorbs more water than that treated at 260 °C due to the relatively increased fraction of lignin. Pretreated biomass solid at 200 °C has not only the highest cellulose and lignin percentages but also some hemicellulose. For this reason, it adsorbs most moisture among all of them. The presence of water is important for the cleavage of acetyl groups to yield acetic acid, which plays the further role of catalyst in the depolymerisation of carbohydrates (autocatalysis) of the process (Boonstra and Tjeerdsma, 2006). The texture of the original fiber in raw loblolly pine is much

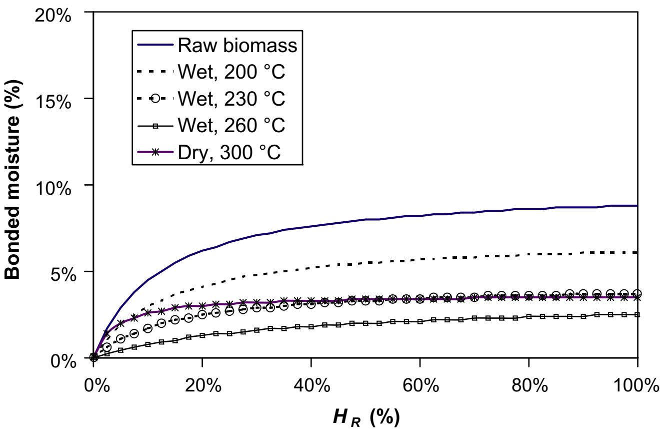

Fig. 3. Effect of relative humidity on bonded moisture in raw and pretreated loblolly.

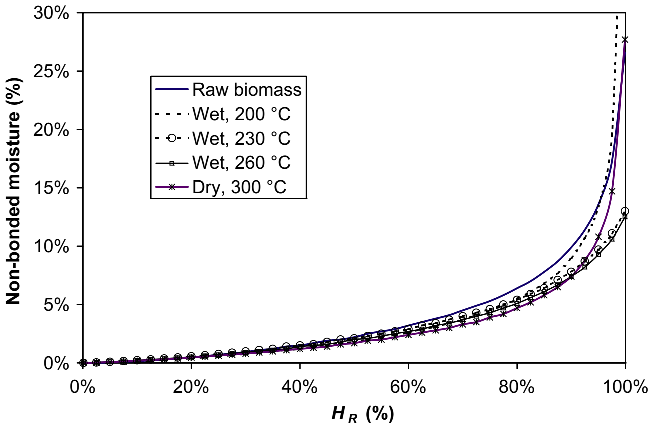

Fig. 4. Effect of relative humidity on non-bonded moisture in raw and pretreated loblolly.

smoother than that of torrefied solids since the original fiber lacks fractures (Yan et al. 2009b, Boonstra, 2008). Thus, the reduced EMC is attributed to reduced binding sites.

In dry torrefaction, the most reactive fraction of biomass, i.e., hemicellulose, degrades as a two-step reaction, in which light volatiles (mono- and polysaccharide fractions and dehydrosugars) are formed in the first step followed by their catalytic degradation (by mineral matter) resulting in the formation of CO and CO_2. When the biomass particles are relatively small, the main part of the acids diffuses out of the particle (Bergman et al., 2005). But unlike the wet torrefaction, some hemicelluloses remain unreacted even at 300 °C and cellulose reacts slowly. Dry torrefaction apparently produces compounds that behave in a manner similar to that of lignin, especially at 300 °C (Yan et al., 2009a). Hemicelluloses, cellulose degradation and further cross linking of lignin make dry torrefied product hydrophobic compare to raw biomass. But the presence of a small amount of hemicelluloses makes it less hydrophobic than the wet torrefied solid product.

As seen in Table 2, the Flory–Huggins binary interaction parameter, χ, decreases with thermal pretreatment. Raw loblolly has $\chi = 3.1$, and is reduced by wet torrefaction with increasing temperature, to 1.2 for treatment at 260 °C. This parameter is normally used to analyze polymer–solvent compatibility. The lower its value, the greater the compatibility between polymer and solvent. $\chi < 0.5$ is the Flory–Huggins theory criterion for a polymer and solvent to be completely miscible over the entire composition range (Ovejero et al., 2007). Higher values of this parameter indicate poor compatibility of water and biomass substrate. Wet pretreatment reduces the degree of insolubility, though it is still high enough to be insoluble in water. In reality, water and biomass substrate are not compatible in these treatment temperature ranges.

In the Flory–Huggins framework, the polymer volume fraction, $\phi_{p,}$ is defined in terms of the fraction of lattice points occupied by the polymer. In the model used in this work, v_{pw} is the ratio of the average specific volume of the biomass with respect to the specific volume of water. The normalized substrate specific volume, v_{pw}, of loblolly pine is 0.15. For dry process it is 0.09 and for wet process, no pattern is obvious in Table 2. The increase of the normalized substrate specific volume indicates the thermal expansion of biomass is faster than that of water. That means the density of dry biomass solid should decrease with an increasing temperature. The skeletal density of solid biomass was found experimentally to be 0.97, 1.16, 1.29 g/cm^3 at treatment temperature of 200, 230, and 260 °C respectively. This density might indicate the pores inside the solid sample may contain pressurized liquid water which has higher density than normal water density. In the Flory–Huggins framework, the assumption that the volume of one solvent molecule and one segment of the polymer chain are equal to one lattice point might be inapplicable in this system due to complex nature of biomass.

The molecular potential energy parameter ($\Delta\varepsilon$) of raw biomass was found to be around -2.13, which is similar to the dimensionless heat of solidification of water (-2.54). Note that the value is negative, indicating that the phase change from the non-bonded phase to the bonded phase releases energy. For the dry process, it is around -3.2 and for wet torrefaction process, the value of $\Delta\varepsilon$ varies from -1.99 to -1.12. This indicates that the phase change energy for moisture between bonded and non-bonded water is more significant in the case of dry torrefied biomass than it is for either raw biomass or wet torrefied biomass.

In general, the model helps to explain some of the physical phenomena of water sorption in woody biomass, but it has some limitations. The EMC model might be improved by accounting for additional molecular interactions and contributions such as pH, ionic conditions, and surface tension. Furthermore, by introducing a better model in place of lattice structure (such as a stochastic distributed network) to describe biomass structure can improve this model (Vasquez and Coronella, 2009).

5. Conclusions

The EMC of pretreated biomass at 30 °C and relative humidities in the range of 11–85% were measured. The EMC of solids produced by either wet or dry torrefaction processes is decreased from that of raw biomass. The EMC of pretreated biomass by wet carbonization decreases with increasing pretreatment temperature, and the wet torrefaction process produces a more hydrophobic solid than the one produced by dry torrefaction. An EMC model was used to analyze the measured data. The physical significance of the four model parameters may be useful in understanding the pretreatment processes. The adsorption capacity decreases significantly with increasing pretreatment temperature.

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